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The Catalytic Conversion of Methyl Chloride to Ethylene and Propylene over Phosphorus-Modified Mg–ZSM-5 Zeolites

YAO SUN,* SHARELLE M. CAMPBELL,* JACK H. LUNSFORD,*,[1]
GREGG E. LEWIS,† DALE PALKE,†,[2] AND LI-MIN TAU†

*Department of Chemistry, Texas A&M University, College Station, Texas 77843; and
†Dow Chemical Company, Freeport, Texas 77541

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A Mg–ZSM-5 zeolite modified with phosphorus is capable of catalyzing the reaction of CH_3Cl to C_2H_4, C_3H_6, C_4H_8, and HCl at 500°C. At a WHSV of 20 h^{-1}, an initial conversion level of 96% was achieved with combined C_2H_4, C_3H_6, and C_4H_8 selectivities of about 80%. During the useful life of the catalyst the C_3H_6 selectivity was 50–60%. The percent conversion decreased to 50% over a period of 20 h, but the catalyst could be regenerated by heating in flowing air. As the catalyst deactivated, the C_3H_6 selectivity increased slightly and the C_2H_4 selectivity decreased. Catalytic and spectroscopic results confirm that phosphorus, derived from trimethylphosphine, was responsible for a decrease in the strong Brønsted acidity in the zeolite. For example, the phosphorus-modified zeolite was inactive for *n*-hexane cracking at 350°C, and the protonated amount of pyridine, added to the zeolite as a probe for acidity, decreased significantly. The catalyst, however, had sufficient acidity to crack hexene or octene at 500°C to propylene and ethylene in ratios that were very similar to those detected during the conversion of CH_3Cl. Without the strong Brønsted acidity the PMg–ZSM-5 zeolite apparently is unable to convert the light olefins to paraffins and aromatics. A mechanism is proposed in which magnesium cations activate CH_3Cl to form HCl and a carbene intermediate. The latter is believed to be responsible for C–C bond formation via reaction with a surface methoxide species. Ethylene probably is the primary hydrocarbon, but it oligomerizes to a higher molecular weight olefin which cracks back to ethylene and propylene.

INTRODUCTION

The utilization of methane to produce more valuable chemicals and fuels has been the subject of intense research during the past decade. Because of their widespread use in the petrochemical industry, ethylene and propylene are two of the most attractive target molecules. The oxidative coupling of methane provides a route for the formation of ethylene; however, current yields of ca. 25% make this process only marginally acceptable for practical use (*1*, *2*). As a consequence, indirect processes are currently being explored. One such process is the reaction of methane and oxygen to syngas, followed by a methanol synthesis step, and finally the conversion of methanol to light olefins (*3–5*). Alternatively, methane may be converted to methyl chloride via an oxychlorination reaction (*6*). Methyl chloride is then transformed into light olefins and hydrochloric acid (*7*, *8*). The latter compound can be recycled for use in the oxychlorination reaction.

The conversions of CH_3Cl and CH_3OH to light olefins have in common the fact that both processes are catalyzed by modified ZSM-5 zeolites. Over a normal H–ZSM-5 catalyst both CH_3Cl and CH_3OH are converted to paraffins, aromatics, cycloparaffins and C_6^+ olefins, presumably via C_2–C_5 olefins (see below) (*9*, *10*). The reactions of CH_3OH over ZSM-5 zeolites to light olefins and higher hydrocarbons has been studied in great detail, with emphasis on the mecha-

[1] To whom correspondence should be addressed.
[2] Present address: Allied Signal Corp., Tulsa, Oklahoma.

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nism for the formation of the first carbon–carbon bond. Although there are undoubtedly many parallels between the reactions of CH_3Cl and CH_3OH over ZSM-5 zeolites, there may be important distinctions in that certain proposed intermediates derived from CH_3OH (CH_3OCH_3, oxonium ions) are not accessible from CH_3Cl. Although there is no compelling reason at present to expect that the mechanisms of the two molecules reacting over ZSM-5 are identical, it is anticipated that research on both will be mutually instructive.

Earlier work on the conversion of CH_3Cl to light hydrocarbons was reported by Jens *et al.* (*7*); however, a more extensive study has recently been described by Lersch and Bandermann (*8*), who examined a number of modified ZSM-5 catalysts for the conversion of CH_3Cl. They found that ZSM-5 which contained Mg^{2+} was the most active of the catalysts studied and had the longest lifetime. It is significant that in both respects Mg–ZSM-5 was superior to H-ZSM-5. The Mg–ZSM-5 catalyst was reasonably selective for the production of light olefins, with the selectivity for propylene being as great as 40 wt%.

Because of the parallels between the reactions of CH_3Cl and CH_3OH over ZSM-5, it is important to point out the earlier work of Kaeding and Butter (*3*) and the more recent study of Dehertog and Froment (*5*) on the conversion of CH_3OH to light olefins. Kaeding and Butter demonstrated that modification of ZSM-5 with phosphorus compounds greatly improved the selectivity for C_2–C_4 olefins, particularly at temperatures > 400°C. They were able to achieve up to 70% selectivity to C_2–C_4 olefins at 100% CH_3OH conversion. Dehertog and Froment studied the effects of a number of factors on light olefin production, including Si/Al ratio, the type of cation, phosphorus modification, and partial pressure. They also found that phosphorus modification significantly increased the C_2–C_4 olefin yield. Higher temperatures and lower pressures of CH_3OH likewise had a positive effect on olefin selectivity.

In the current study emphasis was placed on maximizing the yield of C_2H_4 and C_3H_6 from the reaction of CH_3Cl by modifying ZSM-5 zeolites. It was of interest to determine the roles of phosphorus and Mg^{2+} cations in decreasing the Brønsted acidity of the zeolite and in providing an alternate pathway for reactions to occur. The early work of Chang and Silvestri (*11*) on CH_3OH conversion over H–ZSM-5 suggested that in this strongly acidic material the light olefins react further to form higher molecular weight hydrocarbons. Therefore, one strategy for maximizing the yields of light olefins would be to eliminate the strong acid sites that are responsible for paraffins and aromatics. Lercher and co-workers (*12*) have demonstrated that a phosphorus treatment removes the strong Brønsted acidity, but in doing so it might be expected to reduce the activity as well. Indeed, Dehertog and Froment (*5*) have noted that the addition of trimethylphosphite to a H–ZSM-5 zeolite decreased the activity for CH_3OH conversion. The Mg^{2+} ions may play a role in the activation of CH_3Cl which becomes equally as effective as the protons in the zeolite.

EXPERIMENTAL

Preparation of catalysts. The ZSM-5 zeolites in the ammonium form were supplied by Conteka (CBV1502, CBV5020, and CBV3020), and had bulk SiO_2/Al_2O_3 ratios of 150, 50, and 30. Unless otherwise noted, the material which had a SiO_2/Al_2O_3 ratio of 30 (CBV3020) was used. Magnesium ions were introduced by an ion-exchange method in which 20 g of the zeolite was mixed with 2 liter of aqueous solutions that contained 2.75 wt% $Mg(NO_3) \cdot 6H_2O$. The exchange process was carried out for 8 h at 80°C. The sample is designated Mg–ZSM-5.

Phosphorus was added to the zeolite by adsorbing trimethylphosphine (TMP, Aldrich, 97%). The zeolite was first degassed for 2 h at 400°C under vacuum; then the adsorption was carried out under 50–80 Torr of TMP for 30 min at 25°C. The sample designated PMg–ZSM-5 was degassed for 2 min

at 25°C under vacuum and calcined for 4 h at 600°C in static air. This calcination step in static air is important for obtaining a selective catalyst. The sample was then calcined in flowing air at 600°C for 12 h. It is important that the final calcination step be done immediately prior to use of the catalyst; the fully oxidized catalyst deteriorated on storage under normal laboratory conditions. For one zeolite, designated P(2)Mg–ZSM-5, the process was repeated twice to introduce more phosphorus.

Evaluation of catalytic activity and selectivity. Catalytic reactions were carried out in a fused-quartz U-shaped reactor having an internal diameter of 8 mm. An undiluted bed of 0.1 g of the catalyst (20–45 mesh) was placed on quartz wool in one leg of the reactor. Quartz chips were used to preheat the reactant gas. An external thermocouple was placed adjacent to the catalyst bed. The samples were activated *in situ* under flowing air using the following programmed temperature schedule: 4.5 h to 600°C, 2 h at 600°C, then drop to 500°C over 1 h. A stream of CH_3Cl, diluted with a CH_4/N_2 mixture to yield a CH_4/CH_3Cl ratio of 1.5 was introduced into the reactor. In several experiments only N_2 was used as the diluent, and the results were the same as those obtained using CH_4. The weight hourly space velocity (WHSV) was based on the amount of CH_3Cl that passed over the catalyst. Selectivities are given in mole percent.

The product stream was passed through a cold trap at 0°C to remove condensable hydrocarbons and a solid sodium hydroxide bed to remove HCl. An on-line sampling valve was used to introduce part of the gas stream into a Varian 3700 chromotograph, equipped with a 10-m Hayesep S (80–100 mesh) column. Nitrogen (15%) in methane was used as an internal standard.

Emphasis in this study was placed on C_1–C_4 hydrocarbons; however, in one set of experiments analysis of C_5–C_{10} hydrocarbons was carried out also. In another set of experiments the reaction of ethylene and propylene over the catalysts was tested. The same catalytic conditions and analysis, as for the conversion of methyl chloride, were used for these experiments. Some of the catalysts also were tested for the cracking of *n*-hexane, 1-hexene, and 1-octene. The hexene and octene cracking reactions were carried out in the system described above. A stream of N_2 (20 ml min^{-1}) was passed through a saturator containing hexene at 0°C or octene at 25°C. The extent of hexane cracking was determined at 350°C, using a system described previously (*13*). After activation *in situ* at temperatures up to 400°C, 0.045 g of catalyst was contacted with a stream of hexane diluted in nitrogen. A stream of N_2 (20 ml min^{-1}) was passed through an *n*-hexane saturator at 0°C and then into the catalytic reactor. The conversion of hexane was determined after 5 min on stream.

Characterization. An inductively coupled plasma (ICP) method was used to determine the aluminum, magnesium and phosphorus content of the zeolite. The material was dissolved in a solution of HF and $HClO_4$, heated until dry, dissolved a second time in the acids, heated until dry, and finally dissolved in H_2O.

The zeolites used in the pyridine study were the same as those used in the catalytic experiments. The spectra of these samples were obtained using a Perkin–Elmer 1710 FTIR spectrometer. The zeolites were pressed into self-supporting wafers (ca. 7 mg/cm^2) and activated at 500°C under flowing dry N_2. Spectra were recorded at 150°C with the use of a heatable IR cell. Correction for variation in zeolite wafer thickness was made before plotting of the spectra.

Some of the infrared spectra were obtained using a ZSM-5 zeolite supplied by Professor J. A. Lercher. This material had superior transmission in the hydroxyl stretching region (i.e., 3400–3800 cm^{-1}). Spectra were obtained using a Digilab FTS-40 Fourier transform spectrometer equipped with an MCT detector.

The ^{31}P and ^{27}Al NMR spectra were obtained using a Bruker MSL-300 solid state

NMR spectrometer (7.05 T). Zirconium rotors were filled with about 0.2 g of zeolite. The samples were spun (3 kHz) at the magic angle to remove line broadening caused by homonuclear or heteronuclear interactions. ^{27}Al NMR spectra were recorded for fully hydrated zeolite samples. The peak area of the signal attributed to tetrahedral lattice aluminum was calculated for each of the samples and corrected for sample mass and number of scans. Spectra were compared with that of the H–ZSM-5 zeolite as a standard.

The composition of the near surface region of the zeolites was determined by X-ray photoelectron spectroscopy (XPS) using a Hewlett–Packard Model HP5950A spectrometer with Al $K\alpha$ X rays.

The pore volumes of the catalysts were measured by N_2 adsorption at -196°C. A Quantasorb Jr instrument was used to determine the volume of N_2 adsorbed at $P/P_0 = 0.3$, on samples which had been pretreated by heating to 400°C in flowing He/N_2.

RESULTS AND DISCUSSION

Catalytic results. A preliminary study of H–ZSM-5(30), carried out at a relatively low WHSV of 5 h^{-1} and at 425°C, showed that the lifetime of the catalyst was reasonably good (40% conversion after 30 h), but the selectivity to ethylene and propylene was poor. The C_3H_6 selectivity gradually increased to a level of about 18% while the C_2H_4 selectivity was approximately constant at 3–5%. At a greater space velocity of 20 h^{-1} and at 500°C the decay in activity was more rapid, as shown in Fig. 1; but the combined ethylene and propylene selectivity was considerably improved, especially for the H–ZSM-5(50) zeolite. As shown in Fig. 1b, the half-life of the reaction with the H–ZSM-5(50) catalyst was only ca. 5 h, but the combined ethylene, propylene and butene selectivities varied from 65% at shorter times on stream to 50% after 5 h. The propylene concentration was greater than the ethylene or butene concentrations, even when the catalysts became highly deactivated.

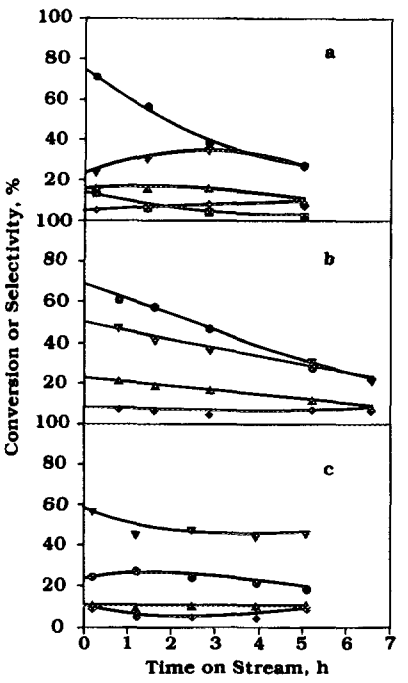


FIG. 1. Reaction of CH_3Cl over (a) H–ZSM-5(30), (b) H–ZSM-5(50), and (c) H–ZSM-5(150) catalysts: ●, CH_3Cl conversion; ▲, C_2H_4 selectivity; ▼, C_3H_6 selectivity; ■, C_3H_8 selectivity; and ◆, C_4H_8 selectivity (T = 500°C and WHSV = 20 h^{-1}).

The half-lives of the H–ZSM-5(30) and H–ZSM-5(150) catalysts were 4 and 5 h, respectively, and the initial activity for H–ZSM-5(150) was less than that observed for the H–ZSM-5(50) catalyst. The crystallinity of the H–ZSM-5(30) zeolite was shown to be good after reaction. ^{27}Al NMR revealed that prior to catalytic use, the amount of tetrahedral aluminum in the H–ZSM-5(30) zeolite was 40% less than in H–ZSM-5(50) zeolite. Thus, the H–ZSM-5(30) zeolite must contain a considerable amount of extraframework aluminum.

The addition of Mg^{2+} to the ZSM-5(30) catalyst significantly improved the initial activity and the lifetime of the catalyst, as was observed previously by Lersch and Bandermann (*8*). They reported nearly 100% conversion over a 3-h period at 425°C and at a WHSV = 3 h^{-1}. Over the Mg–ZSM-5

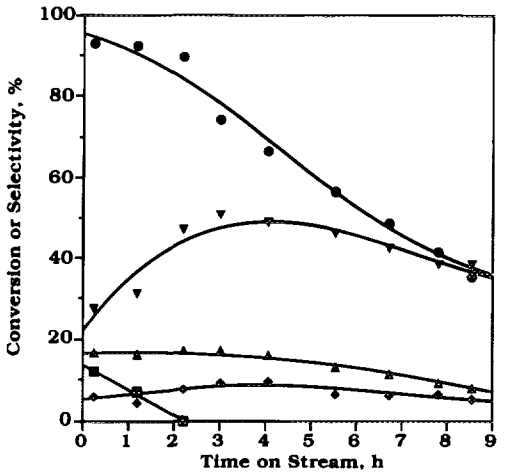


FIG. 2. Reaction of CH_3Cl over Mg–ZSM-5 at 500°C, WHSV = 20 h^{-1}: ●, CH_3Cl conversion; ▲, C_2H_4 selectivity; ▼, C_3H_6 selectivity; ■, C_3H_8 selectivity; and ◆, C_4H_8 selectivity.

catalyst at 500°C and a WHSV = 20 h^{-1} the initial conversion was 95%, but it decreased to 50% after 7 h on stream (Fig. 2). The propylene selectivity increased from 30% to 50% over the same period. These values may be compared to a propylene selectivity of 24% under the conditions of Lersch and Bandermann (*8*).

Further modification of the catalyst by the addition of phosphorus (PMg-ZSM-5) increased the half-life of the catalyst by a factor of almost 3, and increased the propylene selectivity to a level of 50–60%, as shown in Fig. 3a. During the useful life of the catalyst the ethylene selectivity decreased from 16 to 5%, and the butene selectivity remained constant at 7%. Thus, the combined C_2H_4, C_3H_6, and C_4H_8 selectivities were approximately 80%. Analysis including C_5–C_{10} products indicated that no higher alkanes or aromatics were produced at 500°C over the PMg–ZSM-5 zeolite. In terms of catalyst life and light olefin selectivity this material was considerably better than the Mg–ZSM-5 zeolite. A PH–ZSM-5 catalyst had a half-life of only 0.5 h and propylene selectivity of 6%. The WHSV for the latter catalyst was 15 h^{-1}. When additional phosphorus was added to the PMg–ZSM-5 zeolite, the C_2H_4 and C_3H_6 selectivities increased slightly but the CH_3Cl conversion decreased significantly (Fig. 3b).

The PMg–ZSM-5 deactivated catalysts could be completely regenerated by cooling the catalyst to 200°C, introducing a flow of air, heating the catalyst to 600°C at a rate of 100°C h^{-1}, and holding at 600°C for 12 h. Catalysts were deactivated and regenerated up to four times with no loss in initial activity or light olefin selectivity. The catalyst lifetime, however, increased as a result of continued catalytic use and regeneration. The half-life of the catalyst which had been deactivated and regenerated four times was 35 h in comparison with the 20 h half-life of the fresh catalyst. This improvement in catalyst life has been reported previously for

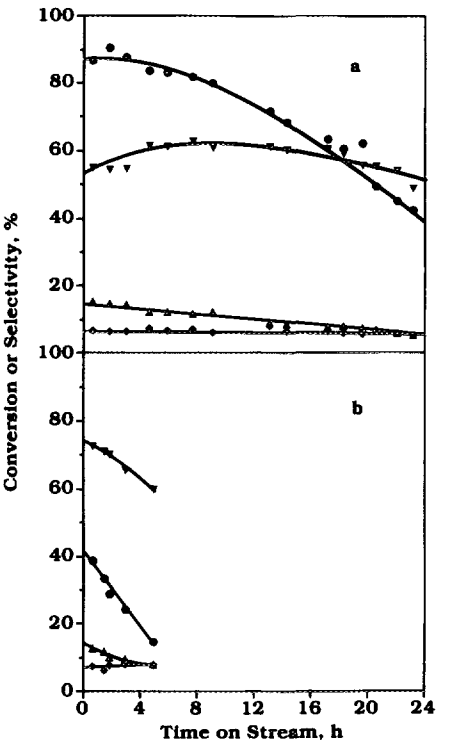


FIG. 3. Reaction of CH_3Cl over (a) PMg–ZSM-5 and (b) P(2)Mg–ZSM-5 catalysts: ●, CH_3Cl conversion; ▲, C_2H_4 selectivity; ▼, C_3H_6 selectivity; and ◆, C_4H_8 selectivity (T = 500°C and WHSV = 20 h^{-1}).

H–ZSM-5 zeolite used in methanol-to-gasoline conversion (*14*).

In an effort to gain insight into the mechanism and the nature of the active centers reactions were carried out using *n*-hexane, 1-hexene, and 1-octene. Hexane cracking has been used extensively to probe strong Brønsted acidity in zeolites (*15–17*). The conversion of hexane over H–ZSM-5, Mg–ZSM-5 and PMg–ZSM-5 zeolites was found to be 18, 19, and 0.3%, respectively. Thus, it is evident that the phosphorus extensively poisoned the strong Brønsted acidity.

For the conversion of CH_3OH to higher hydrocarbons Kaeding and Butter (*3*) have discussed a reaction scheme in which C_2H_4 is oligomerized to higher olefins, which in turn react to form aromatics and paraffins. In addition, the larger olefins may crack back to the lighter olefins. For example, hexene may crack back to propylene. Moreover, it was noted that the presence of phosphorus inhibited the reactions leading to aromatics and paraffins.

We suggest that many of the same general phenomena occur when CH_3Cl reacts in the phosphorus-modified PMg–ZSM-5 zeolites. That is, C_2H_4 is the initial hydrocarbon product, but it oligomerizes to hexene and perhaps octene. The more demanding reactions that would result in aromatic and paraffin formation do not occur, but the hexene and octene are cracked back to propylene and ethylene. In order to support this hypothesis, hexene and octene were separately passed over the PMg–ZSM-5 catalyst. The results are shown in Fig. 4, from which it is evident that the major products were ethylene and propylene. The product distributions obtained with CH_3Cl and hexene were similar. The agreement with the octene result likewise was reasonable. The agreement in product distribution obtained when methyl chloride, hexene, and octene were reacted over H–ZSM-5 or Mg–ZSM-5 was not nearly as good.

The product distributions also were obtained over the PMg–ZSM-5 catalyst using

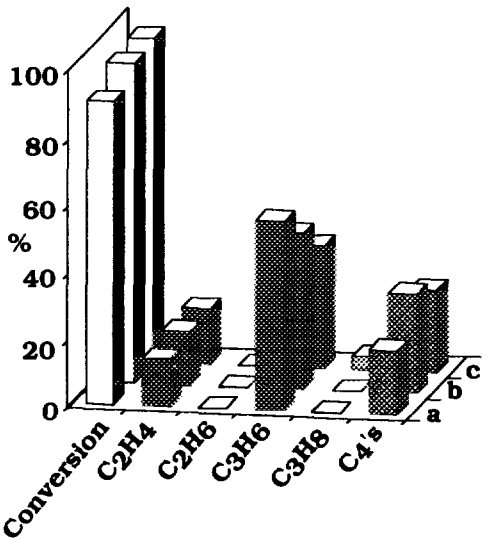


FIG. 4. Conversion and product distribution over a PMg–ZSM-5 zeolite with the reagents (a) CH_3Cl, (b) 1-hexene, and (c) 1-octene at T = 500°C.

ethylene and propylene as the feeds; however, interpretation of the results is complicated by the fact that it is impossible to distinguish between the unreacted alkene and the amount produced as a secondary product. Whereas a reasonable amount of propylene was produced from ethylene (37% C_3H_6 selectivity, assuming 100% C_2H_4 conversion), the amount of propylene detected after propylene reacted was unexpectedly small (only 15% C_3H_6 selectivity, assuming 100% C_3H_6 conversion). When propylene reacted, the major products were C_4 hydrocarbons. It is not apparent why the product distributions were so different, although the results suggest that the treatment with phosphorus altered the acid sites such that the rates of oligomerization and subsequent cracking were decreased, relative to the rates of diffusion out of the zeolite. Thus, the products were influenced by the nature of the original alkene. For example, ethylene may oligomerize only to hexene and octene, while propylene may oligomerize mainly to nonene. These results suggest that ethylene, rather than propylene, is the

major primary product in CH_3Cl conversion.

The role of magnesium and phosphorus in modifying acid centers. H–ZSM-5 zeolites function as strong Brønsted acids, and it is expected that the conversion of CH_3Cl to hydrocarbons would be an acid-catalyzed reaction. But when Mg^{2+} ions are added to the catalyst, the activity increases considerably, as indicated by the results of Figs. 1 and 2, and even more convincingly by the results of Lersch and Bandermann (*8*). The surprising result is that the first addition of phosphorus to the catalyst did not have a strong negative effect on activity. If indeed the phosphorus compound in the zeolite poisoned the acidity, then one must consider another type of site for the activation of CH_3Cl.

Clearly, the acidity of the zeolites becomes a critical factor in understanding the catalytic phenomena. Three methods were used to determine the acidity of the zeolites that were used in this study: the hexane cracking activity as described above, and the IR spectra of hydroxyl groups and adsorbed pyridine.

Infrared studies. The infrared spectra of pyridine adsorbed on H–ZSM-5, Mg–ZSM-5, and PMg–ZSM-5 zeolites, shown in Fig. 5, demonstrate that phosphorus reduces the acidity in the zeolite. The spectrum of pyridine on H–ZSM-5 (Fig. 5a) exhibits the characteristic bands at 1543 and 1456 cm^{-1}, which are attributed to pyridinium ions and Lewis-bound pyridine, respectively (*19*). Following adsorption of pyridine on the Mg–ZSM-5 zeolite (Fig. 5b) the area of the band at 1543 cm^{-1} was reduced by 40%, relative to the same band in the H–ZSM-5 sample, and a new band appeared at 1450 cm^{-1} which is assigned to pyridine coordinated with Mg^{2+} ions (*19*). In the oxidized phosphorus-modified sample (PMg–ZSM-5) there was a further 20% reduction (i.e., total loss of 60% compared with the H–ZSM-5 sample) in the concentration of Brønsted acid sites and a significant loss in the pyridine coordinated with the Mg^{2+} ions (Fig. 5c). Introduction of more phosphorus (P(2)Mg–ZSM-5) led to an additional loss of 15% (Fig. 5d), to yield a total loss of 75% of the Brønsted acidity associated with the H–ZSM-5 zeolite. The amount of pyridine associated with Lewis acid sites and Mg^{2+} ions was very small in this sample, which also had very low activity. It is evident that the effect of the phosphorus in the sample is to reduce the concentration of both pyridinium ions and coordinately bound pyridine.

Although the IR studies shown in Fig. 6 were not carried out on the catalyst samples, the improved transmission in the hydroxyl region provides qualitative information that supports the results obtained with pyridine. The H–ZSM-5 sample exhibited the usual bands at 3745 and at 3605 cm^{-1}, with a shoulder at 3725 cm^{-1} (Fig. 6a). The 3745-cm^{-1} band is assigned to terminal SiOH groups, perhaps on the exterior of the crystal, and the 3605-cm^{-1} band to acidic bridging hydroxyls (*18*). The shoulder at 3725 cm^{-1} has been attributed to internal SiOH groups. The bands in the 1600–2100 cm^{-1} region result from overtones of the framework deformations.

The spectrum of the Mg–ZSM-5 zeolite (Fig. 6b) had the same two major bands, except the intensity of the 3605-cm^{-1} band was reduced by about 15%. An additional band was apparent at 3670 cm^{-1}, which is attributed to $Mg(OH)^+$ ions in the zeolite. A similar band was observed in Mg–Y zeolites (*19*).

When TMP was adsorbed into the Mg–ZSM-5 zeolite (no oxidation) the intensities of all of the hydroxyl bands decreased (Fig. 6c), and new bands appeared at 1300–1450, 1700, 2455, and 2900–3000 cm^{-1}. The positions of these bands are in agreement with those reported by Schoonheydt *et al.* (*20*) following adsorption of TMP in a H–Y zeolite. The band at 2455 cm^{-1}, which occurs in H–Y at 2485 cm^{-1}, is attributed to the protonated TMP adduct, $[(CH_3)_3P–H]^+$. After oxidation of the sample twice in static air at 600°C, the bands

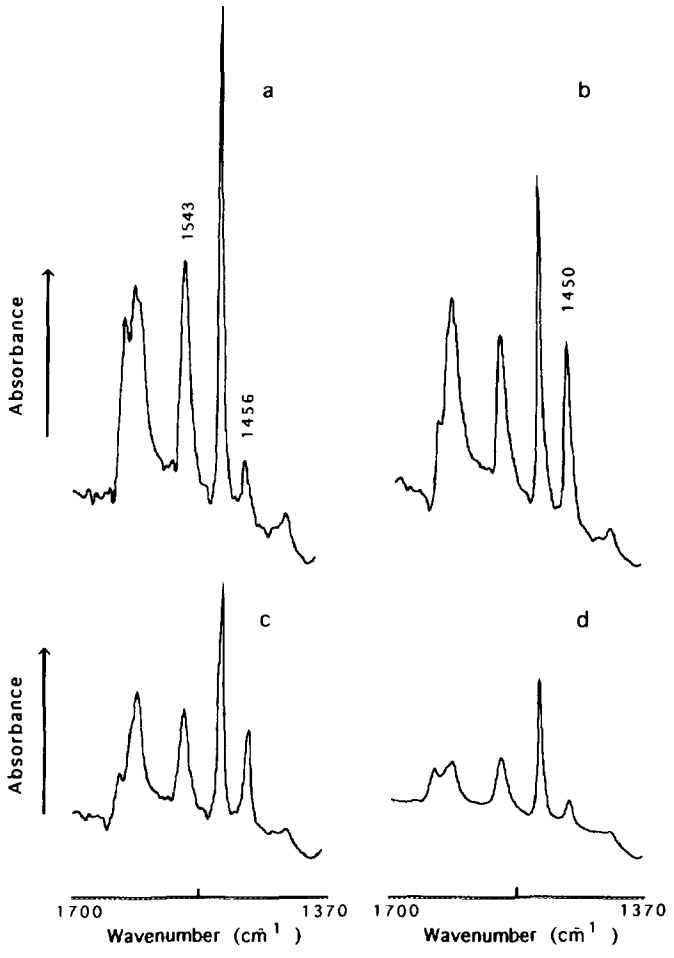


FIG. 5. Infrared spectra of (a) H–ZSM-5(30), (b) Mg–ZSM-5, (c) PMg–ZSM-5, and (d) P(2)Mg–ZSM-5 zeolites after pyridine adsorption; spectra of the respective zeolites before pyridine adsorption have been subtracted.

associated with TMP almost completely disappeared, and the acidic hydroxyl band at 3605 cm^{-1} did not reappear (Fig. 6d). Moreover, when TMP was added to this oxidized sample, the band at 2455 cm^{-1} was very weak (Fig. 6e).

Since HCl is a product of the reaction, it was of interest to determine whether exposure of the oxidized PMg–ZSM-5 zeolite to HCl would introduce acidic hydroxyl groups. In this case the zeolite had only been oxidized once at 600°C after adding the TMP. Following the addition of dry HCl it is evident from spectrum f, Fig. 6, that no hydroxyl groups were produced.

^{31}P NMR studies. Phosphorus-31 NMR has been used to determine the state of the oxidized phosphorus in the zeolite. Oxidation in static air at temperatures up to 600°C resulted in a sharp resonance at 24 ppm. Only weak signals were observed in the 49 to 65 ppm region, which would indicate the formation of trimethylphosphine oxide (*21*). Surprisingly, the ^{31}P resonance at 24 ppm was accompanied by a ^{13}C resonance at 17 ppm, which demonstrates that carbon was present in the zeolite following oxidation at high temperatures. Jentys *et al.* (*18*) found evidence for an organophosphorus species in a H–ZSM-5 zeolite after heating a sample

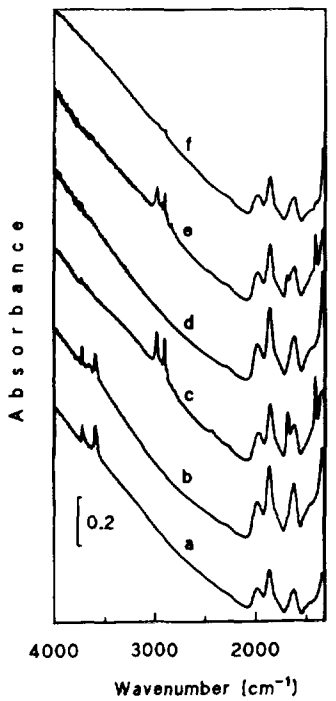


FIG. 6. Infrared spectra of ZSM-5 zeolites: (a) H–ZSM-5, (b) Mg–ZSM-5, (c) Mg–ZSM-5 after adsorption of TMP, (d) Mg–ZSM-5 with TMP after oxidation twice in air at 600°C, (e) after addition of TMP to the oxidized sample, and (f) PMg-ZSM-5 that had been exposed to HCl.

loaded with TMP to 300°C for 12 h in air. The exact nature of the species responsible for the resonance at 24 ppm is not known; however, it is tentatively assigned to an organophosphate compound.

Upon further oxidation of the sample in flowing air at 600°C the resonance at 24 ppm decreased and broader resonances were observed at −13 and −38 ppm. In the fully oxidized PMg–ZSM-5 catalyst only these resonances and a small signal at 0 ppm were detected, as shown in Fig. 7. Seo and Ryoo (*22*) as well as Lischke *et al.* (*23*) have used NMR to study phosphorus-modified H–ZSM-5 zeolites. Both groups reported ^{31}P resonances due to reacted forms of phosphorus between −5 and −40 ppm. Lischke *et al.* (*23*) attributed resonances at −5 and −13 ppm to end and middle groups in pyrophosphates or short chain polyphosphates. Such species may contribute to the broad resonance at low fields in Fig. 7. Lischke *et al.* (*23*) have attributed the resonance at −40 ppm to highly condensed polyphosphates; whereas, Seo and Ryoo (*22*) tentatively assigned this resonance to phosphorus reacting with impurities or vacancies in the zeolite. We favor the former interpretation. The small signal at 0 ppm is assigned to simple monophosphate species.

^{27}Al NMR studies. Aluminum-27 NMR studies of the catalyst samples (Fig. 8) allow one to determine the aluminum content of the lattice following various treatments. Ion exchange with magnesium ions had no effect on the lattice aluminium content (Fig. 8b); the small amount of octahedral aluminum

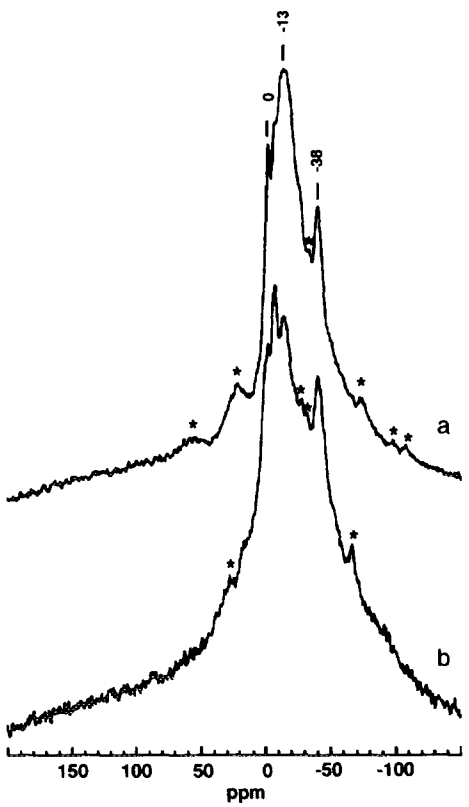


FIG. 7. ^{31}P NMR spectra of (a) PMg–ZSM-5 and (b) P(2)Mg–ZSM-5 catalysts (* denotes spinning side bands).

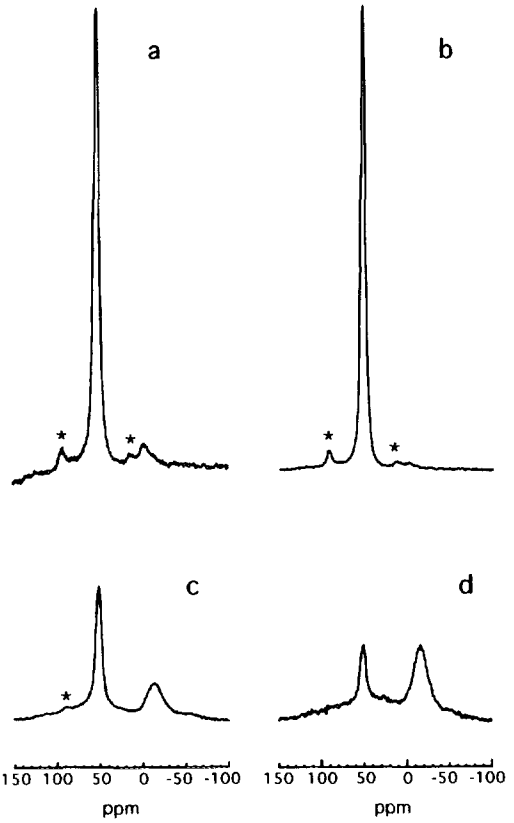


FIG. 8. ^{27}Al NMR spectra of (a) H–ZSM-5(30), (b) Mg–ZSM-5, (c) PMg–ZSM-5, and (d) P(2)Mg–ZSM-5 catalysts (* denotes spinning side bands).

detected in the parent H–ZSM-5 was, however, lost in the washing process. Phosphorus modification and oxidation caused a loss of 50% of the lattice aluminum in the PMg–ZSM-5 sample (Fig. 8c). This loss compares well with the loss of Brønsted acid site concentration. Following the phosphorus modification a signal, accounting for 30% of the aluminum initially in the lattice, appeared at −15 ppm. This signal is attributed to aluminium phosphate extralattice material (*24*). Further addition of phosphorus (P(2)Mg–ZSM-5) led to a sample in which only 20% of the lattice aluminum remained (Fig. 8d). Aluminium as aluminum phosphate amounts to only 20% of the initial lattice aluminium in this sample. Thus, a large portion of the aluminium in these modified samples is "NMR invisible" as a result of the quadrupolar interaction in an unsymmetrical environment (*25*). Clearly, phosphorus modification reduces the Brønsted acidity of the catalyst by dealumination of the lattice and formation of extralattice aluminum and aluminophosphate material.

Further characterization. Both bulk and near-surface analyses were carried out on several of the zeolites used in this study and the results are given in Table 1. From the bulk analysis it appears that the equivalents of Mg exchanged into the zeolite were small compared to the exchange capacity of the zeolite. However, by comparison of the peak area of the tetrahedral lattice aluminum signal in the ^{27}Al NMR spectrum of this sample with that of a standard of known lattice aluminum content, it was determined that only 30% of the total aluminum in this zeolite sample was in the lattice. Therefore, on the basis of the framework aluminum content the sample was in fact extensively exchanged with magnesium ions. The content of phosphorus relative to the content of aluminum is large, indicating that more phosphorus was introduced than that which would be associated with the lattice aluminum sites.

The XPS results given in Table 1 indicate that the H–ZSM-5 and Mg–ZSM-5 samples had equivalent surface and bulk aluminum contents. The Mg^{2+} was enriched at the surface of the Mg–ZSM-5 sample. Following phosphorus modification and oxidation the surface was depleted in aluminum and the Mg/Al ratio increased further. The P/Al ratio of the surface was comparable to that of the bulk.

The amount of N_2 adsorbed in the zeolites at −196°C and $P/P_0 = 0.3$ is listed in Table 1. This is close to the saturation amount of N_2, therefore the calculated volumes may be compared with an estimated free volume of 0.19 $cm^3 g^{-1}$ for H–ZSM-5. The lower value of 0.17 $cm^3 g^{-1}$ for the H–ZSM-5 sample used here can be attributed to the high extralattice aluminium content of this sample. It is evident from the results that the phosphorus re-

TABLE 1

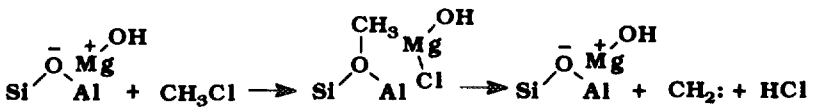
Analyses of Zeolite Catalysts[a]

Catalyst	Bulk analysis[b]			Surface Analysis[c]			N_2 adsorbed at $P/P_0 = 0.3$, −196°C ($cm^3\ g^{-1}$)
	Si/Al	Mg/Al	P/Al	Si/Al	Mg/Al	P/Al	
H–ZSM-5(30)	15	0	0	15	0	0	0.17
Mg–ZSM-5	15	0.15	0	14	0.33	0	0.16
PMg–ZSM-5	15	0.15	0.81	19	0.62	0.64	0.15
P(2)Mg–ZSM-5	15	0.15	1.41	—	—	—	0.13

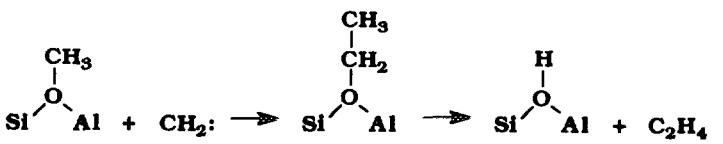
[a] Atomic ratios are given.
[b] Obtained by ICP.
[c] Obtained by XPS.

duces the accessible volume by only a very small amount (10%). This partial blocking of the channels has a small effect on the catalytic activity of the material.

A model for the active site. Under the same catalytic conditions, the conversion of CH_3Cl increased significantly following magnesium modification. The Mg–ZSM-5 catalyst is more active than the H–ZSM-5. After phosphorus modification the high activity persisted even though much of the acidity had been destroyed. Both of these observations indicate that Mg^{2+} ions are involved in the activation of CH_3Cl. We propose that ethylene is formed by the following mechanism:



(1)



(2)

The surface proton would then react with another CH_3Cl molecule to form HCl and a methoxide group. Evidence for the formation of methoxide comes from the ^{13}C NMR spectrum following reaction of the zeolites with $^{13}CH_3Cl$ for 10 min at 275°C in a closed system. In both H–ZSM-5 and Mg–ZSM-5 a resonance was observed at 48 ppm, which is assigned to methoxide species. Methanol has a ^{13}C resonance at 51 ppm, therefore following the adsorption of methanol there is ambiguity concerning the assignment of a resonance in this region to methoxide groups or methanol. However, following the adsorption of methyl chloride only methoxide groups could be responsible for this resonance. Methyl chloride itself exhibits a ^{13}C resonance at 25 ppm, as determined from the adsorption of $^{13}CH_3Cl$ in H–ZSM-5 at 25°C. Methoxide groups also were detected in a PMg–ZSM-5 zeolite, although the amplitude of the signal was less than that found in the H–ZSM-5 and Mg–ZSM-5 zeolites.

According to the above mechanism a carbene intermediate is involved in the formation of C–C bonds via addition to the surface methoxide. Evidence for the role of a carbene intermediate in the formation of pri-

mary products has been reviewed by Chang (*10*) and by Hutchings and Hunter (*26*). This mode of C–C bond formation during the conversion of methanol to hydrocarbons was previously proposed by Lee and Wu (*27*). More recently attention has been given to the role of an oxonium ylide in generating C–C bonds; however, the formation of an oxonium ylide usually requires the presence of dimethyl ether, which, of course, is not produced during the reaction of methyl chloride in the zeolite.

It is possible that propoxide species, formed by the insertion of a second carbene, are directly responsible for the production of propylene, although with propylene as the feedstock a very different product distribution was observed from that obtained using either CH_3Cl or C_2H_4 as the feed. It seems unlikely therefore, that propylene is a major primary product. This variation in the mechanism cannot be excluded, but the observed propylene and ethylene can be adequately accounted for by the oligomerization–cracking reactions described previously.

CONCLUSIONS

The addition of both Mg^{2+} ions and phosphorus to a ZSM-5 zeolite gives catalysts which are both active for the conversion of CH_3Cl and selective for the formation of propylene and, to a lesser extent, ethylene and butene. These positive effects also are accompanied by a greater lifetime of the catalyst before deativation. It is evident from this and related studies that Mg^{2+} ions enhance the activity of the catalyst, and phosphorus effects the improved selectivity. Both Mg^{2+} ions and the phosphorus affect the lifetime of the catalyst. Test reactions and spectroscopic studies confirm that the phosphorus in the zeolite decreases the strong Brønsted acidity of the catalyst. These strongly acidic Brønsted sites are believed to be responsible for the formation of paraffins and aromatics, which in this particular case are undesirable reactions that result in liquid products. The Mg^{2+} or perhaps $Mg(OH)^+$ ions at exchange sites in the zeolite may activate CH_3Cl through the formation of a Mg–Cl bond, with the concomitant formation of a methoxide species. According to the proposed model these surface intermediates decompose to form a carbene and HCl. The carbene is believed to react with other methoxide ions to produce the initial C–C bonds. This part of the mechanism is identical to one proposed previously to explain the formation of C–C bonds from CH_3OH over H–ZSM-5 zeolites. Additional carbene insertion steps may yield propoxide ions, which decompose to propylene. More likely, ethylene, the initial hydrocarbon product, oligomerizes and cracks back to the observed distribution of propylene and ethylene.

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